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Basic polyhedral clusters have been derived from intermetallic compounds at near-eutectic composition by considering a dense packing and random arrangement of atoms at shell sites. Using such building units, bulk metallic glasses can be formed. This strategy was verified in the Cu–Zr binary system, where we have demonstrated the existence of Cu_8Zr_5 icosahedral clusters in $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ amorphous alloys. Furthermore, ternary bulk metallic glasses can be developed by doping the basic Cu–Zr alloy with a minority element. This hypothesis was confirmed in systems $(Cu_{0.618}Zr_{0.382})_{100-x}Nb_x$, where $x=1.5$ and 2.5 at. %, and $(Cu_{0.618}Zr_{0.382})_{98}Sn_2$. The present results may open a route to prepare amorphous alloys with improved glass forming ability. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2213020]

Since the discovery of glassy systems, based on multicomponent alloys, in the early 1990s, bulk metallic glasses (BMGs) have been extensively studied because certain mechanical properties, such as strength, can be significantly improved over their crystalline counterparts.[1–11] BMGs produced so far usually contain three or more elements.[1–3] Until now, complex compositions have been considered necessary in order to inhibit crystallization of the liquid phase during cooling of the melt. However, simpler systems should be of great interest, fundamentally as well as technologically, since they would facilitate the atomic-structure determination for a given BMG, which has been a long-standing problem.[12–24] Originally, the dense-random-packed model was used to describe metallic glasses.[25] This model is based on the assumption that the glass consists of a random arrangement of spherical atoms (hard spheres) of each element. However, it has also been pointed out that localized, directional chemical bonding and the formation of groups of atoms are relevant factors to theories of glass formation and stability.[26] The local structure is well defined and similar to that of the crystalline form of the material. Recently, a topological model for metallic glass formation was proposed.[27,28] According to that model, a solute occupying either substitutional or interstitial sites in the host lattice can destabilize the lattice by producing a critical internal strain. Besides the structural models mentioned above, several criteria for structural stability of a BMG have been suggested: (1) large value of the reduced glass transition temperature T_g/T_l, where T_g is the glass transition temperature and T_l is the liquidus temperaure;[29] (2) three empirical rules for a large supercooled liquid region: (a) multicomponent system, (b) significant differences in atomic size, and (c) negative heats of mixing among the main constituent atoms;[1,3] (3) high gamma value, $\gamma=T_x/(T_g+T_l)$, where T_x is crystallization temperature;[30] (4) interaction between the Fermi surface and the Brillouin zone in a nearly-free-electron model;[31] (5) the critical concentration of a solute element required for amorphization decreases, reaches a minimum, and then increases with increasing ratio between the size of the solute and the solvent atoms;[27,32,33] (6) there is an optimum ratio R^* between the size of the solute atom and the average size of the surrounding solvent atoms for dense packing.[28,34] In spite of the criteria mentioned above, the design of alloys with a high glass forming ability (GFA) remains to a large extent unpredictable due to lack of understanding of the local atomic structure. Although polyhedral clusters have been revealed in some metallic glasses,[12–20] more efforts are still needed to uncover the atomic structure of a given BMG and to predict compositions with high GFA. In this letter, we report a method of designing appropriate polyhedral units to simulate the local atomic structure of binary Cu–Zr amorphous alloys. Our method predicts the formation of Cu_8Zr_5-based BMGs, in which the polyhedral units are indeed experimentally detected.

We have chosen the Cu–Zr binary system as a prototype because of three reasons: (1) it has a wide composition range forming metallic glasses, (2) BMGs can be formed in this system,[35] and (3) its phase diagram is known. There are several intermetallic compounds, Cu_5Zr, $Cu_{51}Zr_{41}$, Cu_8Zr_3, $Cu_{10}Zr_7$, CuZr, and $CuZr_2$. The Wykoff sites of Cu and Zr in these compounds are listed in Pearson's handbook.[36] Taking

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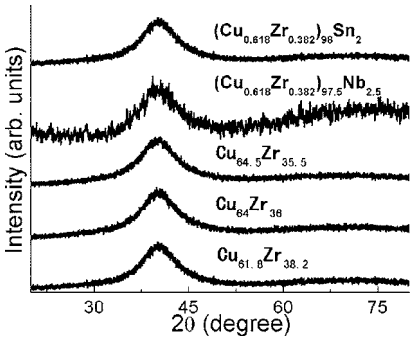

FIG. 1. X-ray diffraction patterns for the as-spun Cu–Zr metallic glasses and as-cast 3 mm $(Cu_{0.618}Zr_{0.382})_{97.5}Nb_{2.5}$ and $(Cu_{0.618}Zr_{0.382})_{98}Sn_2$ BMG rods.

each Wykoff site as the center, 35 polyhedral one-shell clusters can be constructed using the computer program ATOMS.[37] In order to select appropriate clusters as basic units for the forming of BMGs, three factors have been considered: (1) dense packing, (2) random arrangement of atoms at shell sites, and (3) near-eutectic composition. Dense packing is an essential criterion for the atomic structure of BMGs.[38] Suppose that the radius of the center atom in a cluster is r_0 and that the average radius of the shell atoms is r_1, according to Miracle[28] and Miracle and Sanders,[34] the ratio $R=r_0/r_1$ should be within 10% from the optimum value R^* for close packing. Clusters with less than ten atoms were not considered in the present work since $r_{Cu}/r_{Zr}=0.79$, which is 10% larger than the optimum value $R^*=0.71$ for a solute atom surrounded by nine solvent atoms. Based on a random arrangement of atoms, the concentration of atoms of the same kind on shell sites might lead to instability of the cluster. Finally, 11 clusters out of a total of 35 were selected for further study. There are four eutectic points of interest in the present work: $Cu_{61.8}Zr_{38.2}$, $Cu_{56}Zr_{44}$, $Cu_{45.7}Zr_{54.3}$, and $Cu_{27.6}Zr_{72.4}$. As it turns out, three of our selected clusters, namely, Cu_8Zr_5 ($Cu_{61.5}Zr_{38.5}$), Cu_6Zr_5 ($Cu_{54.5}Zr_{45.5}$), and Cu_5Zr_6 ($Cu_{45.5}Zr_{54.5}$), are very close to eutectic compositions. BMG rods have recently been synthesized with compositions $Cu_{64.5}Zr_{35.5}$ (with a diameter of 2 mm), $Cu_{64}Zr_{36}$ (with a thickness of 2 mm), $Cu_{60}Zr_{40}$ (with a diameter of 1 mm), and $Cu_{45}Zr_{55}$ (with a diameter of 1.5 mm).[35] This fact strongly suggests that polyhedral clusters are the main building units of Cu–Zr BMGs with near-eutectic compositions. Two key questions will be addressed in the present work: (1) Do polyhedral clusters exist in BMGs based on the Cu–Zr system? (2) If yes, will it be possible to predict other cluster-based BMGs, in which the value of R is made close to R^* by alloying with a minority element? To answer these questions, three compositions, $Cu_{61.8}Zr_{38.2}$ (eutectic composition), $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$, were selected. As will be shown below, extended x-ray absorption fine structure (EXAFS) measurements at the Cu and Zr K absorption edges indicate that the metallic glasses indeed contain Cu_8Zr_5 icosahedral clusters. Moreover, BMG rods with a diameter of 3 mm could be produced with a minor addition of Nb and Sn, making R closer to R^*.

Cu–Zr ingots with compositions $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ were prepared by arc melting of high-purity metals (99.8%–99.9%). Ribbons with a cross section area of 0.03×2.5 mm^2 were obtained by single-roller melt spinning at a wheel surface velocity of 30 m/s in purified argon atmosphere. The x-ray diffraction (XRD) patterns (cf. Fig. 1) consist of a broad peak at $2\theta\approx40°$, confirming the amorphous state. EXAFS measurements at photon energies corresponding to the Cu and Zr K absorption edges were performed at the HASYLAB synchrotron radiation source (beamline X1) in transmission. Standard data evaluation was carried out using the VIPER and WINXAS programs.[39] In the fitting process, the FEFF-8 code[40] was used to calculate scattering amplitudes and phases.

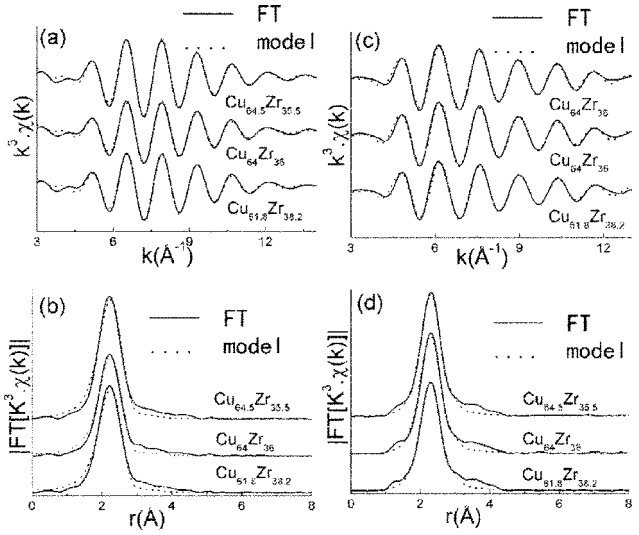

FIG. 2. EXAFS spectra in k space and r space for as-spun Cu–Zr metallic glasses. Full curves denote experimental measurements; dotted curves are the result of the fit using the model described in the text. (a) and (b) at the Cu K edge; (c) and (d) at the Zr K edge.

In Fig. 2 we show Cu and Zr K-edge EXAFS spectra for as-spun $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ metallic glasses. A Cu_9Zr_4 icosahedral cluster with a Cu atom at the center position and a Cu_8Zr_5 icosahedral cluster with a Zr atom at the center (Fig. 3) were designed as models for the fits to the experimental Cu and Zr K-edge spectra, respectively. Cu–Zr and Zr–Cu bond distances were forced to be equal during the fitting. As shown in Fig. 2, the observed Cu and Zr K-edge spectra in k and r spaces are well described by the fitting curves. The EXAFS fitting parameters are given in Table I. It is clear that the Cu center atom is indeed surrounded by about five Zr and seven Cu atoms, forming a Cu_8Zr_5 icosahedral cluster, although the Cu_9Zr_4 model was used as the initial input. Slight differences between the Cu–Cu and Cu–Zr bond lengths indicate a distorted icosahedral cluster with a Cu atom at the center site. On the other hand, the Zr atom is found to have only about four Cu atoms

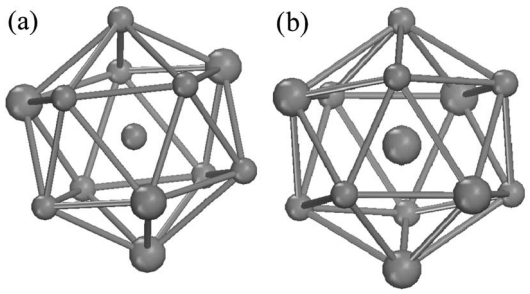

FIG. 3. Icosahedral models for EXAFS simulation. Small spheres are Cu atoms and large spheres are Zr atoms. (a) Cu at center position for simulation of Cu K-edge spectra; (b) Zr at center position for simulation of Zr K-edge spectra.

TABLE I. EXAFS results. N is the coordination number, r_{i-j}, where i and j are Cu and/or Zr, is the interatomic distance, and σ^2 is the mean-square relative displacement. In order to minimize the number of parameters, a single energy shift was varied for each absorption edge.

		r_{i-j} (Å)		N		σ^2 (10^{-3} Å)	
Alloy	Atom at center	–Cu	–Zr	–Cu	–Zr	–Cu	–Zr
$Cu_{61.8}Zr_{38.2}$	Cu	2.53(2)	2.68(7)	7(2)	5(2)	26(4)	13(1)
	Zr	2.68(7)	3.01(3)	4(2)	8(2)	9(1)	29(1)
$Cu_{64}Zr_{36}$	Cu	2.53(2)	2.69(7)	7(2)	5(3)	26(4)	12(1)
	Zr	2.69(7)	3.01(3)	4(2)	8(2)	9(1)	28(2)
$Cu_{64.5}Zr_{35.5}$	Cu	2.53(2)	2.69(7)	7(3)	5(3)	24(4)	13(1)
	Zr	2.69(7)	3.00(3)	4(2)	8(2)	9(1)	27(2)

as nearest neighbors, while the Zr–Zr coordination number is about 8. The results above imply that Cu atoms are situated at the center sites of Cu_8Zr_5 icosahedral clusters, while the Zr atoms are located at the shell sites. This is understandable, since the radius of the Cu atom (1.28 Å) is less than the radius of the Zr atom (1.61 Å). Various ways of combining Cu-centered Cu_8Zr_5 icosahedral clusters may result in slight differences in the composition of the alloy. Thus, our results strongly support the hypothesis above that the atomic structure of $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ amorphous alloys is mainly made up of Cu_8Zr_5 icosahedral clusters.

Adding a third element, having a larger atomic radius than Cu, at shell sites of the Cu_8Zr_5 icosahedral clusters should result in a higher R value and thereby a higher GFA.[28,34] Consequently, one would expect a whole class of Cu_8Zr_5-based BMGs according to our model. In order to test this hypothesis, we have selected Nb (atomic radius of 1.47 Å) and Sn (atomic radius of 1.51 Å) as the minority elements and prepared amorphous alloys according to the formulas $(Cu_{0.618}Zr_{0.382})_{98.5}Nb_{1.5}$, $(Cu_{0.618}Zr_{0.382})_{97.5}Nb_{2.5}$, and $(Cu_{0.618}Zr_{0.382})_{98}Sn_2$. It is found that BMG rods with a diameter of 3 mm could indeed be produced (Fig. 1) by copper mold.

In conclusion, basic polyhedral clusters have been derived for intermetallic compounds at near-eutectic composition by considering a dense packing and random arrangement of atoms at shell sites. Using such building units, BMGs can be formed. This strategy was verified in the Cu–Zr binary system, where we have demonstrated the existence of Cu_8Zr_5 icosahedral clusters in $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ amorphous alloys. Furthermore, ternary BMGs can be developed by doping the basic Cu–Zr alloy with a minority element. This hypothesis was confirmed in systems $(Cu_{0.618}Zr_{0.382})_{100-x}Nb_x$, where $x=1.5$ and 2.5 at. %, and $(Cu_{0.618}Zr_{0.382})_{98}Sn_2$. The present results may open a route to prepare amorphous alloys with improved GFA.

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[40] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58**, 7565 (1998). To account for many-electron excitations, we took the many-body factors S_o^2 as calculated by FEFF. The instrumental broadening was included into FEFF calculations by adjusting the imaginary part of the scattering potential in a way that we could extract the true coordination numbers ($N=12$) from the reference EXAFS spectra of pure Cu and Zr foils. Then the same broadening was used for the calculations of interest.